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Influence of tungsten ion valence states on electrical characteristics of quaternary lithium-antimony-lead-germanate glasses

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ABSTRACT

Effect of adding WO_3 into $Li_2O–Sb_2O_3–PbO–GeO_2$ glasses on dielectric properties *viz.*, dielectric constant, ε′(ω), loss, tan δ, ac conductivity, σ_{ac}, and electric moduli, M(ω), over a wide range of frequency *viz.*, 0.01 Hz to 1 MHz and in temperature range from 303 to 523 K have been studied. Ac and dc conductivities as well as dielectric parameters exhibited the lowest values at 3.0 mol% of WO_3. Quantum mechanical tunneling (QMT) is used for the analysis of ac conductivity. The variations of dc conductivity, analyzed by small polaron hoping model, are explained in terms of variations in the redox ratio of tungsten ions. Relaxation dynamics was investigated using electrical modulus formalism and such effects are attributed to the formation of $W^{5+}O^{3-}$ complexes. The structural modifications in the glass network have been quantitatively analyzed by IR, optical absorption and EPR spectroscopic studies.

1. Introduction

Germanium oxide, is a good glass former which possesses superior optical properties like high refractive index (~2.14) and large transmission in the NIR region [1–3]. This is a reason that the germanium oxide based glasses are being extensively used in IR technology, nonlinear optics, in the design of laser devices and for light guiding core of optical fiber [4,5]. Further, germanate glasses mixed with alkali oxides like Li_2O are interesting candidates for solid electrolyte applications [6] since they exhibit high ionic conductivity. Several recent studies on the structural aspects of germanium oxide glasses indicated that network of these glasses consists of GeO_4 and GeO_6 structural units [7–11]. When germanium oxide glasses are mixed with another metal oxide *viz.,* Sb_2O_3 that exhibits large electrical polarizability, their applications are extended on three-dimensional photonic devices for integrated optics and other nonlinear optical devices such as ultrafast optical switches, power limiters, broad band optical amplifiers [12,13]. In general, antimony oxide participates in the glass network with SbO_3 structural units and form the cross links with GeO_4 and GeO_6 structural units. Recently, we have reported the influence of different modifier oxides *e.g.*, PbO, ZnO, BaO, CaO, SrO *etc.*, on the electrical properties of lithium antimony germanate glasses. These studies indicated that glasses mixed with PbO exhibited superior electrical properties [14].

Physicochemical and electrical properties of antimony germanate glasses can be improved to a large extent if they are mixed with interesting transition metal oxides like WO_3. In several recent studies, it has been reported that the addition of WO_3 to different amorphous materials, makes them to show photochromism. For this reason these glasses are reported to be useful for applications in information display devices of high memory, in smart windows to control solar input of buildings [15–18].

The electrical properties of antimony germanate glasses are also expected to be influenced extensively by tungsten ions since these ions exist in different valence states *viz.*, W^{6+}, W^{5+} and W^{4+} as per the following thermo-reversible disproportionate reaction $W^{5+}+W^{5+}\leftrightarrow W^{4+}+W^{6+}$ [19–21]. Usually, W^{6+} ions participate in the glass network with different structural units like WO_4 (T_d) and WO_6 (O_h), whereas W^{5+} ions form the complexes of the type $W^{5+}O_3^-$ and occupy octahedral positions. With the insertion of WO_4 and WO_6 structural units inside the covalent germanate chains, physical properties, especially electrical properties, are expected to be changed to a large extent.

Most of the studies available on WO_3 mixed glasses are restricted to photochromism and other related spectroscopic properties. The study of electrical properties such as dielectric constant, ε, loss tan δ and ac conductivity, σ_{ac}, dc conductivity, σ_{dc}, using impedance spectra over a

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wide range of frequency and temperature of the glass materials not only helps in understanding the conduction phenomenon but also gives information which can be correlated with structural changes in glass network [22,23]. Such perceptive information is highly helpful for widening the scope of these materials for applications in solid state batteries as electrolytes. This study is devoted to have a broad understanding over the topology and valence states of tungsten ions and their influence on electrical characteristics of $Li_2O–Sb_2O_3–PbO–GeO_2$ glass system. The obtained results were analyzed with aid of other auxiliary studies that include optical absorption, EPR and IR spectroscopy.

2. Experimental

The detailed compositions of the glasses (in mol%) used in the present study are as follows:

W_0: $10Li_2O–30Sb_2O_3–20PbO–40GeO_2$
W_1: $10Li_2O–29Sb_2O_3$ – $20PbO–40GeO_2$: $1WO_3$
W_2: $10Li_2O–28Sb_2O_3–20PbO–40GeO_2$: $2WO_3$
W_3: $10Li_2O–27Sb_2O_3–20PbO–40GeO_2$: $3WO_3$
W_4: $10Li_2O–26Sb_2O_3–20PbO–40GeO_2$: $4WO_3$
W_5: $10Li_2O–25Sb_2O_3–20PbO–40GeO_2$: $5WO_3$

Analytical grade reagents of Li_2CO_3, Sb_2O_3, GeO_2, PbO, WO_3 (Sigma Aldrich 99.99% pure) powders in appropriate proportions were thoroughly mixed in an agate mortar and melted in a silica crucible at 1300 °C in a PID temperature controlled furnace for about 20 min until a bubble free liquid was formed. The resultant bubble free melt was then poured in a brass mold and subsequently annealed at 400 °C.

A programmable VIBRA HT density measurement kit is used to determine the densities of the bulk samples automatically (with readability 0.0001 g/cm^3) by means of Archimedes' principle with O-Xylene (99.9% pure) as buoyant liquid. The samples were then grounded and optically polished. The final dimensions of the samples used for the present measurements were about 1.0 cm×1.0 cm×0.1 cm. The optical absorption spectra of the samples were recorded in the wavelength range of 300–900 nm up to a resolution of 0.1 nm using JASCO V-670 UV–Vis NIR spectrophotometer. FTIR transmission spectra were recorded on a JASCO-FT/IR–5300 spectrophotometer to a resolution of 0.1 cm^{-1} in the range of 400–1200 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). The EPR spectra of the fine powders of the samples were recorded at room temperature on JEOL JES-TES100 X–band EPR spectrometer.

For electrical measurements gold electrodes were sputtered onto both sides of the samples using sputter coater SC7620. Dielectric properties were measured using an impedance analyzer (Novocontrol Alpha-AN Dielectric Spectrometer) over a frequency range from 0.01 Hz to 1 MHz and in temperature range from 303 to 523 K. The temperature was controlled to an accuracy of ± 0.5 K. Calculation of σ(ω) was performed separately using the experimental data and sample dimensions. The parameters of the equivalent circuits were obtained by the complex non-linear least square (CNLLSQ) fitting directly to the measured impedance data. The values of the resistance, R and the sample dimensions were used to evaluate the dc conductivity.

3. Results

From the measured values of the density *d* and average molecular weight *M* of the samples, various physical parameters such as tungsten ion concentration, N_i, mean tungsten ion separation, R_i and also polaron radius, R_P(=1/2*(π/6N_i)^1/3)), for $Li_2O–Sb_2O_3–PbO–GeO_2$: WO_3 glass samples were calculated and presented in Table 1. The density of the samples is observed to increase slightly with increasing WO_3 content.

Fig. 1 represents the dispersion of real part of dielectric constant, ε′(ω), *vs.* frequency at different temperatures for W_1 glass. At higher frequency ε′(ω) seems to approach a constant value, ε′$_\infty$(ω). Fig. 2 shows the variation of ε′(ω) with temperature at different frequencies for W_2 glass. To understand the influence of WO_3 concentration on dielectric constant of the studied glasses, we have presented a comparison plot of variation of dielectric constant with frequency measured at 523 K in Fig. 3. This temperature, 523 K, was selected because all experimental spectra for glasses investigated are well defined at higher temperatures. The minimal value of dielectric constant was found for glass containing 3.0 mol% of WO_3 (inset of Fig. 3).

Fig. 4 represents the dispersion of imaginary part of dielectric constant, ε′′ (ω) *vs.* frequency at different temperatures for $Li_2O–Sb_2O_3–PbO–GeO_2$ glass containing 3.0 mol% of WO_3. Inset of Fig. 4 shows ε′′(ω) *vs.* frequency for different samples measured at 523 K. Fig. 5 shows the dispersion of imaginary part of dielectric constant, ε′′(ω) *vs.* temperature at different frequencies for $Li_2O–Sb_2O_3–PbO–GeO_2$ glass with 4.0 mol% of WO_3.

Fig. 6(a) shows the isotherms of ac conductivity, σ_{ac}, *vs.* frequency for W_5 glass, whereas Fig. 6(b) exhibits the variation of σ_{ac} with $1/T$ at different frequencies. At higher temperatures and lower frequencies, conductivity is observed to be independent on frequency and considered to be the dc conductivity, σ_{dc}. With increasing frequency, the conductivity increased in a nearly power law fashion. On the other hand, at the lowest temperatures, in our experimental frequency window, the dc conductivity is not observed, the conductivity is strongly frequency- and weakly temperature- dependent.

Fig. 7 shows the variation of ac conductivity, σ_{ac}, *vs.* 1/T for the glasses with different concentrations of WO_3 at high frequency, 131.68 kHz, at where the bulk properties are expected to dominate. The activation energy, W_{ac}, for conductivity, in the linear part at high temperatures in these graphs, is determined and presented in Table 5. A considerable decrease of conductivity with increase in the concentration of WO_3 up to 3.0 mol% at any given temperature is observed. The value for W_{ac} is found to be the highest for W_3 sample.

From the values of dc resistance, R, obtained from fitting analysis and sample dimensions, we have evaluated dc electrical conductivity, σ_{dc}, for all the glasses and its variation with $1/T$ in the temperature range 423–523 K is presented in Fig. 8(a). The variations of dc conductivity and the activation energy, W_{dc}, (evaluated from Arrhenius plots (Fig. 8(a)) with WO_3 content are presented in Fig. 8(b)). The conductivity exhibited the minimal whereas the activation energy maximal value at 3.0 mol% of WO_3.

The variation of dielectric loss or imaginary part of dielectric constant does not exhibit any relaxation effects. To understand the relaxation phenomenon on the dielectric constant and loss, we have evaluated real and imaginary electric moduli, M′(ω) and M″(ω), using real and imaginary parts of complex dielectric constant, ε*:

$$M^* = 1/\varepsilon^*(\omega) = M'(\omega) + i\,M''(\omega), \tag{1}$$

$$\text{here } M'(\omega) = \frac{\varepsilon'(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon''(\omega))^2} \tag{2}$$

$$\text{and } M''(\omega) = \frac{\varepsilon''(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon''(\omega))^2} \tag{3}$$

Fig. 9(a) and (b) represent M′(ω) and M″(ω) spectra for the glass W_5; the figure indicated relaxation behavior. The plots drawn for other glass samples have exhibited a similar behavior.

To have some understanding over the temperature influence on the mobility of the conducting ions (Li^+ ions in this case) the impedance spectra were plotted for the titled glasses. Fig. 10(a) represents impedance spectra for W_4 glass at different temperatures up to 453 K; in the inset of the same figure the impedance spectra for the same glass drawn at high temperatures (from 483 to 523 K) are presented. The comparison plots of impedance spectra measured at 483 K for all the glasses are presented in Fig. 10(b). It is clearly visible